

THEORETICAL STUDIES ON UNSATURATED
COMPOUNDS CONTAINING SULFUR

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DEDICATION

To my wife and to my father

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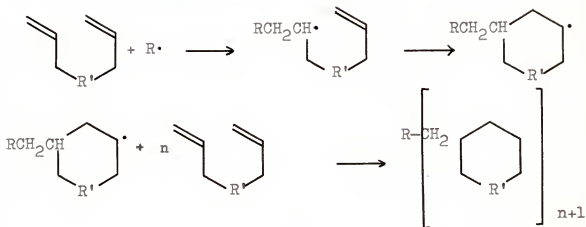
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CHAPTER I

INTRODUCTION

The work in this laboratory of Butler and Ingley (1) uncovered a seeming exception to Staudinger's (2) widely accepted hypothesis that a non-conjugated diene yields exclusively a cross-linked polymer: diallyl quaternary ammonium salts polymerized with free radical initiators to yield water-soluble, non-crosslinked polymers. Subsequent work (3,4) confirmed the anomaly.

Though work (5,6,7,8,9) both before and after that of Butler and Ingley included observations bearing on cyclization during polymerization of such dienes, it remained for Butler and Angelo (10) to postulate a mechanism; namely, intramolecular-intermolecular polymerization (since, also called cyclopolymerization):



The postulate was strongly supported by the subsequent work of Butler, Crawshaw and Miller (11), who studied the degradation products of poly-(diallylammonium bromide) and poly-(diallyldimethylammonium bromide).

Although Butler (12) has proposed across-space homoconjugation as an explanation for the strong tendency of 1,6-dienes to cyclopolymerize, the experimental evidence which does tend to support such an interpretation is offset by other evidence which does not (13).

Therefore, in the present study, the following objectives were decided upon:

- a. to obtain a series of six unsaturated sulfones, each having two double bonds; namely, divinyl sulfone, vinyl allyl sulfone, diallyl sulfone, allyl 3-butenyl sulfone, vinyl 3-butenyl sulfone, and di-3-butenyl sulfone,
- b. to determine whether the sulfones, as examined in the UV, visible and IR portions of the spectrum, show any signs of homoconjugation,
- c. to polymerize certain members of the series and examine the polymers via IR.

CHAPTER II

PREPARATION OF THE SULFONES

A. General

As intermediates in the preparation of the sulfones were used, as received, the following materials: allyl mercaptan and diallyl sulfide, Monomer-Polymer Labs; 2-mercaptoethanol, K and K Laboratories, Inc.; 3-butene-1-ol (experimental sample), Tennessee Eastman Research Laboratories. The divinyl sulfone, purchased from Union Carbide and Chemicals Co., and the ethylene chlorohydrin, purchased from Matheson, Coleman and Bell, were re-distilled before use.

In the course of the syntheses, certain physical constants were recorded: boiling points (in uncorrected degrees centigrade at pressures in millimeters), refractive indices (as determined on a Bausch and Lomb Abbe 34 Refractometer), and, in some cases, densities. IR spectra were run, variously, on three instruments: a Perkin-Elmer Model 221 Prism-Grating Spectrophotometer, a Beckman IR-5a, and a Perkin-Elmer Infracord. All elemental analyses were run by Galbraith Laboratories, Inc.

B. Divinyl sulfone

A commercially obtained sample was re-distilled, giving a fraction having the following physical constants:

b.p. $101^{\circ}/9.4$ mm, $n_D^{21} = 1.4749$, $d_4^{21} = 1.1782$; lit. (14),

b.p. $107.6^{\circ}/14.5$ mm, $n_D^{27} = 1.4737$.

C. Vinyl allyl sulfone

1. Successful route

The vinyl allyl sulfone was prepared according to the procedure of Cope and co-workers (15) and had the following physical constants: b.p. $74-75^{\circ}/0.7$ mm, $n_D^{20} = 1.4835$, $d_4^{20} = 1.1472$; lit. (15), b.p. $80-83^{\circ}/0.7$ mm, $n_D^{25} = 1.4815$, $d_4^{25} = 1.1427$. Reduction at atmospheric pressure, using 5 per cent rhodium on carbon catalyst, of 0.1291 g (0.978 mM) of the sulfone required 44.0 ml (1.96 mM) of hydrogen gas at STP (43.8 ml, calculated).

2. Unsuccessful routes

To avoid the half-mustard gas intermediate in the above preparation, two additional routes to the sulfone were originally attempted: pyrolysis at 515° of 2-acetoxyethyl allyl sulfone (14), and decomposition in alcohol potassium hydroxide solution of the tosyl ester of 2-allylmercaptoethanol (16).

Though pyrolysis of impure 2-acetoxyethyl allyl sulfone did not give the desired product, it is felt that intermediates in the preparation of this sulfone have sufficiently different physical characteristics from those found in the literature to warrant their inclusion:

2-allylmercaptoethanol, b.p. 84-87°/9.9-10.0 mm, $n_D^{24} = 1.5056$. Analysis calculated for $C_5H_{10}OS$: C, 50.80%; H, 8.53%; O, 13.54%. Found: C, 50.80%; H, 8.70%; O, 13.54%. Lit. (17), b.p. 90-92°/12 mm, $n = 1.5079$. 2-acetoxyethyl allyl sulfide, b.p. 79-82°/4.95-5.00 mm, $n_D^{21} = 1.4786$. Analysis calculated for $C_7H_{12}O_2S$: C, 52.49%; H, 7.55%; S, 20.02%. Found: C, 52.55%; H, 7.71%; S, 20.18%. Lit. (17), b.p. 94.5-96°/12 mm, $n = 1.4824$. Experimental difficulties prevented purification of the 2-acetoxyethyl allyl sulfone, which boiled at about 120°/0.04 mm.

The desired reaction of 2-hydroxyethyl allyl sulfide with p-toluene sulfonyl chloride to give a tosyl ester (16) did not occur; instead, the -OH was replaced by -Cl to give 0.05 mole (6.83 g), a yield of 29.6%, of 2-chloroethyl allyl sulfide, b.p. 72-72.2/20-20.2 mm, $n_D^{21} = 1.5054$. Analysis calculated for C_5H_9SCl : C, 43.96%; H, 6.64%; S, 23.47%. Found: C, 44.12%; H, 6.84%; S, 23.46%. Lit. (17), b.p. 67.5-69°/12 mm, $n_D^t = 1.5078$.

At this point it was decided to proceed through the half-mustard gas.

D. Diallyl sulfone

Oxidation of commercially obtained diallyl sulfide, using hydrogen peroxide in an acetic acid medium according to the procedure of Backer et al. (18), gave the sulfone, b.p. 97-101°/2 mm, $n_D^{20} = 1.4893$, $d_4^{20} = 1.1202$; lit. (19), b.p. 109°/3 mm, $n_D^{20} = 1.4893$, $d_4^{20} = 1.1215$.

E. Vinyl 3-butenyl sulfone

1. Successful route

The synthesis of this sulfone comprised four steps: the preparation of 2-hydroxyethyl 3-butenyl sulfide, 2-chloroethyl 3-butenyl sulfide, 2-chloroethyl 3-butenyl sulfone and, finally, vinyl 3-butenyl sulfone.

2-Hydroxyethyl 3-butenyl sulfide was prepared according to the procedure of Fehnel and Garmack (20): the sodium mercaptide of 1.0 mole (78.13 g) of 2-mercapto-ethanol reacted with 1.0 mole (135.0 g) of 1-bromo-3-butene (prepared according to the procedure of Juvala (21)) to give, after fractional distillation through a one foot heated column packed with extruded packing, 0.549 moles (72.5 g), a yield of 54.9%, of a colorless liquid, b.p. 74.8-75°/2.4-2.5 mm, $n_D^{19.5} = 1.4985$. Analysis calculated for $C_6H_{12}OS$: C, 54.50%; H, 9.15%; O, 12.10%. Found: C, 54.38%; H, 9.18%; O, 12.31%.

2-Chloroethyl 3-butenyl sulfide was prepared according to the method of Hurd and Fowler (22): a pyridine solution of 0.336 mole (44.36 g) of 2-hydroxyethyl 3-butenyl sulfide reacted with 0.406 mole (48.2 g) of thionyl chloride to give, after fractional distillation through a one foot heated column packed with extruded packing, 0.202 mole (30.30 g), a yield of 62.0%, of a clear, colorless liquid, b.p. 76-78°/8 mm, $n_D^{19} = 1.5006$. Analysis calculated for $C_6H_{11}SCl$: C, 47.82%; H, 7.36%; Cl, 23.53%; S, 21.27%. Found: C, 47.87%; H, 7.48%; Cl, 23.46%; S, 21.54%.

Oxidation of the sulfide with hydrogen peroxide according to Pomerantz and Connor (23) gave a material which was not characterized, but was, instead, dehydro-halogenated in an impure state: the solvent was removed under water vacuum and the residue dried over anhydrous sodium sulfate.

Vinyl 3-butenyl sulfone was prepared according to the method of Alexander and McCombie (24): approximately 0.2 mole (based on the 0.2 mole of 2-chloroethyl 3-butenyl sulfide oxidized) of 2-chloroethyl 3-butenyl sulfone reacted with 0.21 mole (21.2 g) of triethylamine in dry benzene to give, after bulb-to-bulb distillation, 0.0976 mole (14.27 g), a yield of 48.8%, of vinyl 3-butenyl sulfone, b.p. 69-70°/0.05 mm, $n_D^{19.5} = 1.4808$, $d_4^{19.5} = 1.1085$.

Analysis calculated for $C_6H_{10}O_2S$: C, 49.29%; H, 6.90%; S, 21.93%. Found: C, 49.16%; H, 6.81%; S, 21.69%.

Reduction at atmospheric pressure, using 5% rhodium on carbon catalyst, of 0.1746 g (1.20 mM) of the sulfone required 53.8 ml (2.40 mM) of hydrogen gas at STP (53.6 ml calculated).

2. Unsuccessful routes

Again wishing to avoid a half-mustard gas, intermediate in the above preparation, two routes to the sulfone were originally essayed: pyrolysis at 515° of 2-acetoxyethyl 4-acetoxybutyl sulfone and decomposition in alcoholic potassium hydroxide solution of the tosyl ester of 2-hydroxyethyl 3-butenyl sulfone. Methods of preparation and physical constants of intermediates to the unsuccessfully pyrolyzed 2-acetoxyethyl 4-acetoxybutyl sulfone follow.

2-Hydroxyethyl 4-acetoxybutyl sulfide was prepared according to the procedure of Fehnel and Carmack (20): the sodium mercaptide of 1.0 mole (78.13 g) of 2-mercaptoethanol reacted with 1.0 mole (150.6 g) of 4-chlorobutyl acetate (25) to give 0.163 mole (31.41 g), a yield of 16.3%, of a clear, liquid, b.p. $106-110^\circ/0.07-0.08$ mm, $n_D^{20} = 1.4852$. Analysis calculated for $C_8H_{16}O_3S$: C, 49.96%; H, 8.39%; O, 24.96%. Found: C, 49.49%; H, 8.02%; O, 24.13%.

2-Acetoxyethyl 4-acetoxybutyl sulfide was prepared according to the procedure of Clayton and Reid (26):

2-hydroxyethyl 4-acetoxybutyl sulfide (0.250 mole, 48.07 g) reacted with acetic anhydride (0.300 mole, 30.2 g) to give, after distillation through a one foot heated column packed with protruded packing, 0.225 mole (52.6 g), a yield of 89.7%, of a clear fluid, b.p. 104-107°/0.05-0.06 mm, $n_D^{25} = 1.4693$. Analysis calculated for $C_{10}H_{18}O_4S$: C, 51.26%; H, 7.74%; O, 27.32%. Found: C, 51.36%; H, 7.56%; O, 27.27%.

Experimental difficulties prevented the purification of 2-acetoxyethyl 4-acetoxybutyl sulfone (23), an impure sample of which boiled at approximately 150°/0.04 mm.

The attempted preparation of a tosyl ester via the reaction (17) of 2-hydroxyethyl 3-butenyl sulfone and p-toluene sulfonyl chloride failed; instead, 14.19 g of a clear liquid, b.p. 73-75°/8.5-9.0 mm, $n_D^{20} = 1.5000$, resulted. Analysis calculated for 2-chloro-3-butenyl sulfide, $C_6H_{11}SCl$: C, 47.82%; H, 7.36%; S, 21.27%. Found: C, 48.85%; H, 7.92%; S, 21.70%.

F. Allyl 3-butenyl sulfone

Allyl 3-butenyl sulfide was prepared by the procedure of Fehnel and Carmack (20): the sodium mercaptide of 0.25 mole (18.5 g) of allyl mercaptan reacted with 0.25 mole (33.75 g) of 1-bromo-3-butene (21) to give, after distillation through a 23 plate spinning band column, 0.0628 mole

(8.05 g), a yield of 25.3%, of a clear liquid, b.p. 84-86.5°/64-65 mm, $n_D^{22.5} = 1.4836$. Analysis calculated for $C_7H_{12}S$: C, 65.63%; H, 9.45%; S, 25.03%. Found: C, 65.61%; H, 9.45%; S, 25.06%.

Allyl 3-butenyl sulfone was prepared according to the procedure of Pomerantz and Connor (23): the oxidation of 0.153 mole (19.6 g) of the corresponding sulfide with 30% hydrogen peroxide gave, after bulb-to-bulb distillation, 9.0 g (0.0562 mole), a yield of 36.8%, of a colorless liquid, b.p. 82-84°/0.05 mm, $n_D^{20} = 1.4856$, $d_4^{20} = 1.0876$. Analysis calculated for $C_7H_{12}O_2S$: C, 52.48%; H, 7.55%; S, 20.01%. Found: C, 52.78%; H, 7.54%; S, 20.31%. Reduction at atmospheric pressure, using 82.5% platinum oxide catalyst, of 0.1464 g (0.914 mM) of the sulfone required 40.4 ml (1.80 mM) of hydrogen gas at STP (41.0 ml, calculated).

G. Di-3-butenyl sulfone

Di-3-butenyl sulfide was prepared according to Butler and Price (27) and had the following physical constants: b.p. 75-76°/17 mm, $n_D^{19} = 1.4800$; lit., b.p. 78-80°/17 mm, $n_D^{25} = 1.4825$.

Di-3-butenyl sulfone was prepared according to Pomerantz and Connor (23): di-3-butenyl sulfide (0.150 mole, 21.4 g) reacted with an excess of 30% hydrogen

peroxide to give, after bulb-to-bulb distillation, 0.096 mole (16.72 g), a yield of 64.1%, of a clear liquid, b.p. 89-91°/0.04 mm, $n_D^{20.5} = 1.4823$, $d_4^{20.5} = 1.0633$. Analysis calculated for $C_8H_{14}O_2S$: C, 55.15%; H, 8.10%; S, 18.37%. Found: C, 54.73%; H, 8.21%; S, 18.67%. Reduction at atmospheric pressure, using 82.5% platinum oxide catalyst, of 0.1569 g (0.901 mM) of the sulfone required 40.2 ml (1.80 mM) of hydrogen gas at STP (40.3 ml, calculated).

CHAPTER III

SPECTRAL EXAMINATION OF THE SULFONES

A. General

When the present investigation was undertaken, it was considered desirable to determine whether the sulfones showed any signs of homoconjugation. Accordingly, IR and UV spectra were run, and specific exaltations were calculated.

The IR spectra were run on two instruments: a Perkin-Elmer 221 and a Beckman IR-5a. The former was used to obtain higher resolution spectra of the sulfones in the 5.5-9.25 μ region; the latter was used to obtain survey spectra in the 2-15 μ region.

Because of the unavailability in this laboratory of far UV spectrophotometer, attempts were made to have UV spectra in the 165-250 $m\mu$ region run commercially; the attempts failed. Accordingly, the UV phase of the investigation had to be abandoned.

The refractive indices of the several sulfones, both pure and in dioxane solution, were obtained using a Bausch and Lomb Abbe 34 Refractometer. Densities were obtained using an A. H. Thomas Gay-Lussac type specific gravity

bottle of 1 ml capacity. The refractive indices and densities were all taken in a constant temperature room at $20^{\circ} \pm 2$. An effort was made to determine as nearly simultaneously as possible the refractive index and density of each sample.

Because of the apparent differential exaltation observed, NMR spectra of the sulfones were run: they were obtained using a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer. All of the interpretations were made by Dr. W. S. Brey and his co-workers.

B. Infrared region

The Perkin-Elmer 221, containing the sodium chloride-prism grating interchange, was operated under the following conditions: slit program, 900 (1x); attenuation, 10.0; source current, 0.40 a. The gain was set higher than is usual and the spectrum was recorded at a speed permitting one to assign the counter wavelength of maximum absorption to the peaks. The Beckman IR-5a was operated at standard settings of gain, etc. All samples were run as films between sodium chloride plates.

The Perkin-Elmer 221 was used to examine the 5.5-9.25 μ region, which contains, at approximately 6.1 μ , the C=C stretching wavelength, and the 7.6 μ and 8.8 μ S-O stretching wavelengths. No trend which could be attributed to across space conjugation was discernable.

Below are recorded the wavelengths of the IR absorption peaks and their corresponding relative heights for the six sulfones. Abbreviations used for peak heights are: V.W., very weak; W., weak; M., medium and S., strong. Those wavelengths given to two decimal places are accurate to 0.01μ (as determined with a standard polystyrene film); other wavelengths are accurate to 0.05μ .

TABLE 1
DIVINYL SULFONE

<u>$\lambda(\text{in } \mu)$</u>	<u>Relative Height</u>
3.2	W.
4.4	V.W.
5.1	V.W.
5.84	V.W.
6.19	W.
7.23	M.
7.62	S.
7.99	M.
8.85	S.
9.8	M.
10.2	M.
12.8	S.
14.0	M.

TABLE 2
VINYL ALLYL SULFONE

<u>$\lambda(\text{in } \mu)$</u>	<u>Relative Height</u>
3.2	W.
3.3	W.
5.73	V.W.
6.08	W.
6.19	V.W.
7.03	W.
7.20	W.
7.62	S.
7.99	W.
8.38	W.
8.86	S.
9.26	W.
9.8	M.
10.1	M.
10.6	M.
11.4	W.
12.5	M.
12.9	W.
13.5	M.
14.4	M.

TABLE 3
DIALLYL SULFONE

<u>$\lambda(\text{in } \mu)$</u>	<u>Relative Height</u>
3.4	W.
6.08	W.
7.02	W.
7.15	W.
7.60	S.
7.73	M.
7.98	W.
8.36	W.
8.84	S.
9.23	M.
10.1	M.
10.6	M.
11.5	W.
12.7	W.

TABLE 4
ALLYL BUTENYL SULFONE

<u>$\lambda(\text{in } \mu)$</u>	<u>Relative Height</u>
3.2	W.
3.4	W.
5.4	V.W.
5.6	V.W.
6.08	M.
6.91	W.
7.03	M.
7.61	S.
7.63	S.
7.75	S.
8.01	W.
8.34	W.
8.84	S.
9.24	M.
10.0	M.
10.7	M.
11.3	M.
13.8	W.

TABLE 5
DIBUTENYL SULFONE

<u>$\lambda(\text{in } \mu)$</u>	<u>Relative Height</u>
3.2	W.
3.4	W.
5.83	W.
6.06	M.
6.93	M.
7.08	W.
7.65	S.
7.89	S.
8.10	W.
8.41	W.
8.86	S.
9.2	W.
10.0	M.
10.9	M.
12.2	M.

TABLE 6
VINYL BUTENYL SULFONE

<u>$\lambda(\text{in } \mu)$</u>	<u>Relative Height</u>
3.2	W.
3.4	W.
6.08	M.
6.18	V.W.
6.93	W.
7.21	M.
7.64	S.
8.12	W.
8.43	W.
8.85	S.
9.22	M.
9.8	M.
10.8	M.
12.3	M.
13.2	M.
13.8	M.

C. Visible region

The molar refraction of a compound is given by the familiar Lorentz-Lorenz equation (28),

$$[R] = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

(where n = refractive index, M = molecular weight, and d = density), the value of $[R]$ depending only upon the wavelength of light used in measuring the refractive index. Although theoretically it would be preferable to use light of a wavelength great enough to include the effects of nuclear motion but exclude the effect of permanent dipole orientation, in which case the molar refraction would

represent the actual molar volume, experimental difficulties involved in the use of very long wavelength light, e.g., infrared, make necessary a compromise: light of some definite, shorter wavelength is used (frequently, the sodium D line). Furthermore, the molar refraction, if measured using light of very long wavelength, would be equal to the sum of the requisite atomic and/or structural refraction equivalents similarly determined; because it is not so measured, the equality is only approximate.

In addition to the effect on the equality caused by measuring the refractive index at a wavelength shorter than that approaching infinite wavelength, another factor affects the absolute value of the difference between the observed and the calculated molar refractions: anomalous refractive dispersion.

The index of refraction of a medium, measured at a single wavelength, is given by the equation (28)

$$n = 1 + \frac{a}{\nu_0^2 - \nu^2} \quad ,$$

where a = a constant, ν_0 = the characteristic frequency of the oscillator and ν = the frequency of the single wavelength. As long as

$$\nu \ll \nu_0 \quad ,$$

the refractive index does not change appreciably with a

change in ν . However, in the vicinity of an absorption band of the molecule

$$\nu \longrightarrow \nu_0,$$

and the refractive index begins to increase rapidly, resulting in the above-named anomaly. Saturated organic molecules, and, to a first approximation, molecules not containing a conjugated system of double bonds, do not exhibit the anomaly (also called optical exaltation), because the absorption bands of such molecules are in the far UV. Thus, exaltation suggests itself as a means of determining whether a molecule contains a system of conjugated double bonds.

In the present study, the molar refraction referred to the sodium D line (hereinafter called MRD) of each sulfone was calculated from the corresponding experimentally determined index of refraction and density, using the Lorentz-Lorenz equation. Then, using the sodium D line carbon, hydrogen and double bond refraction equivalents of Eisenlohr (28) and the helium line sulfone group refraction equivalent of Strecker and Spitaler (29), the MRD of each sulfone was calculated. Finally, the exaltation (E) and the specific exaltation (ΣE) (30) of each sulfone were calculated according to the equations below:

$$E = \text{MRD}_{\text{exp.}} - \text{MRD}_{\text{calc.}}$$

$$\Sigma E = \frac{E \times 100}{\text{M.W.}}$$

The sodium D line refractive index, density, experimentally determined MRD, calculated MRD, exaltation and specific exaltation of each sulfone are given in Table 7.

From the table, the empirical nature of MRD calculations becomes evident; the optical depressions (31) suffered by Nos. 1, 2, 5 and 6 are difficult to explain. Perhaps they can be rationalized as being due to an imprecise sulfone group refraction equivalent. In any case, the E values show a definite maximum corresponding to No. 3, diallyl sulfone. That the maximum is affected by molecular weight is shown by the ΣE values, which show a smaller maximum. A graph of the specific exaltation suffered by each sulfone is given in Figure 1.

Despite the relatively greater exaltation evidenced by the diallyl sulfone, considerable doubt as to the validity of the results remained: structural conclusions drawn from MRD calculations most frequently involve exaltations greater than one unit. Therefore, it was necessary to effect an increase, in some way, in the magnitude of the observed exaltations to the extent that they would no longer be in the realm of experimental error.

TABLE 7
VALUES LEADING TO EXALTATIONS EXHIBITED BY THE PURE SULFONES

Compound	n_D^t	d_4^t	MRD (exp)	MRD (calc)	E	E
1. Divinyl sulfone	1.4749 ²¹	1.1782 ²¹	28.23	28.35	-0.12	-0.10
2. Vinyl allyl sulfone	1.4835 ²⁰	1.1472 ²⁰	32.93	32.97	-0.04	-0.03
3. Diallyl sulfone	1.4896 ²⁰	1.1202 ²⁰	37.71	37.58	0.13	0.09
4. Allyl butenyl sulfone	1.4856 ²⁰	1.0876 ²⁰	42.27	42.20	0.07	0.04
5. Vinyl butenyl sulfone	1.4808 ^{19.5}	1.1085 ^{19.5}	37.52	37.58	-0.06	-0.04
6. Dibutenyl sulfone	1.4823 ^{20.5}	1.0633 ^{20.5}	46.74	46.82	-0.08	-0.05

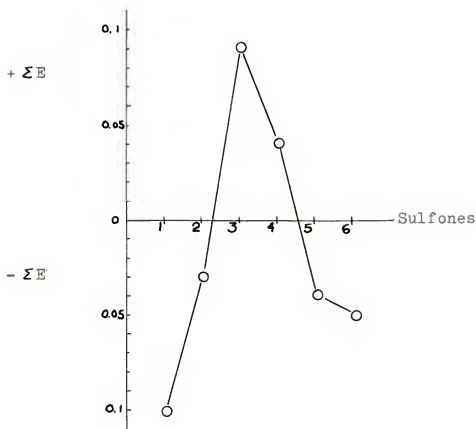


Fig. 1.-Specific exaltations of pure sulfones.

According to Glasstone (32), the relation between the experimentally determined molar refraction $[R]_{1,2}$ of a mixture of x_1 mole fractions of a substance of molecular weight M_1 and x_2 mole fractions of a substance of molecular weight M_2 is given by

$$[R]_{1,2} = \frac{n^2-1}{n^2+2} \cdot \frac{x_1 M_1 + x_2 M_2}{\rho} ,$$

where n and ρ refer to the mixture. The molar refraction is also equal to the sum of the contributions of the constituents, or

$$[R]_{1,2} = x_1 [R]_1 + x_2 [R]_2 .$$

Thus, if the molar refraction of one of the constituents is known, and the molar refraction of the mixture is determined, calculation of the molar refraction of the other constituent is possible.

Reasoning that any existing intramolecular conjugation is decreased to the extent that proximate double bonds in other molecules interfere, the decision was made to determine whether diallyl sulfone (chosen because it showed the greatest exaltation) showed any change in exaltation with decreasing concentration. Accordingly, five solutions of diallyl sulfone in dioxane were made and the density and refractive index of each determined. Use of the equations

above and an MRD for dioxane ($n_d^{20} = 1.4224$ and $d_4^{20} = 1.0338$) of 21.676 gave the results shown in Tables 8 and 9. The curve resulting from plotting ΣE values vs x_1 values is shown in Figure 2.

Three factors influenced the next decision made, which was to compare the exaltations exhibited by 1.5 mole per cent solutions of the sulfones in dioxane:

1. The increasing experimental difficulties encountered in preparing ever more dilute solutions of diallyl sulfone in dioxane.
2. The decreasing supply of two of the sulfones.
3. The lack of any indication that the exaltation suffered by diallyl sulfone was approaching a limiting value.

Accordingly, an approximately 1.5 mole per cent solution of each sulfone in dioxane was prepared and the density and refractive index thereof measured. Then, using the requisite equations above, the MRD (exp.), E , and ΣE values of each sulfone were calculated. The results are given in Tables 10 and 11. Figure 3 is a graph of the ΣE values given in these tables.

That the differential exaltation exhibited by diallyl sulfone in Figure 3 can no longer be considered as possibly due to experimental error seems clear. What is not clear is its cause. Unfortunately, the exaltation

TABLE 8
CONCENTRATIONS: SOLUTIONS OF DIALLYL SULFONE IN DIOXANE

Diallyl sulfone		Dioxane	
grams	moles	grams	moles
x_1		x_2	
--	--	--	0.0
1.0125	0.006926	0.2637	0.002992
1.4599	0.009986	0.8830	0.01002
0.1996	0.001365	2.0207	0.02294
0.0994	0.000680	2.0064	0.02277
0.1246	0.0008523	5.0099	0.05687
			0.9853

TABLE 9
SOLUTIONS OF DIALLYL SULFONE IN DIOXANE:
VARIATION OF EXALTATION

x_1 (sul- fone)	n_D^t	d_4^t	$[R]_1$	E	E
1.0	1.4896 ²⁰	1.1202 ²⁰	37.71	0.13	0.09
0.6983	1.4763 ²¹	1.1046 ²¹	37.71	0.13	0.09
0.4997	1.4650 ²¹	1.0896 ²¹	37.78	0.20	0.14
0.05618	1.4283 ²¹	1.0411 ²¹	37.97	0.39	0.27
0.0290	1.4254 ²¹	1.0360 ²¹	39.18	1.60	1.10
0.01477	1.4240 ²¹	1.0339 ²¹	40.97	3.39	2.32

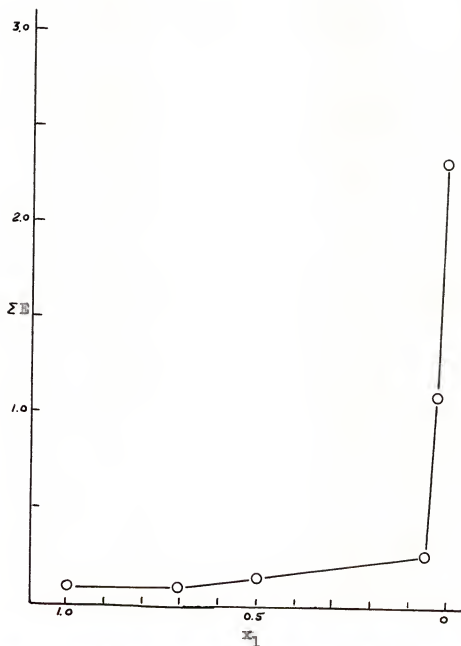


Fig. 2.-Variation of the specific exaltation of diallyl sulfone as a function of concentration.

TABLE 10
CONCENTRATIONS: SOLUTIONS OF THE SULFONES IN DIOXANE

Compound	Sulfone			Dioxane		
	grams	moles	mole fraction x_1	grams	moles	mole fraction x_2
1. Divinyl sulfone	0.1026	0.0008684	0.01502	5.0142	0.05692	0.9850
2. Vinyl allyl sulfone	0.1100	0.0008322	0.01442	5.0105	0.05687	0.9856
3. Diallyl sulfone	0.1246	0.0008523	0.01477	5.0099	0.05687	0.9853
4. Allyl butenyl sulfone	0.1383	0.0008631	0.01496	5.0063	0.05683	0.9851
5. Vinyl butenyl sulfone	0.1337	0.0009145	0.01581	5.0169	0.05694	0.9842
6. Dibutenyl sulfone	0.1473	0.0008454	0.014655	5.0075	0.05684	0.9855

TABLE 11

VALUES LEADING TO EXALTATION EXHIBITED BY THE SULFONES IN DIOXANE SOLUTIONS

Compound	n_D^t	d_4^t	MRD (exp)	MRD (calc)	\bar{v}	\bar{v}
1. Divinyl sulfone	1.4230 ²²	1.0361 ²²	27.50	28.34	-0.85	-0.74
2. Vinyl allyl sulfone	1.4233 ²²	1.0349 ²²	33.70	32.97	0.73	0.55
3. Diallyl sulfone	1.4240 ²¹	1.0339 ²¹	40.97	37.58	3.39	2.32
4. Allyl butenyl sulfone	1.4241 ^{21.5}	1.0353 ^{21.5}	42.57	42.20	0.37	0.23
5. Vinyl butenyl sulfone	1.4232 ^{22.5}	1.0347 ^{22.5}	37.19	37.58	-0.39	-0.27
6. Dibutenyl sulfone	1.4237 ^{21.5}	1.0329 ^{21.5}	48.10	46.82	1.28	0.74

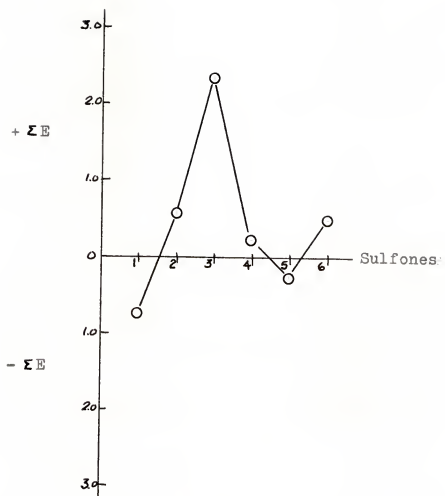


Fig. 3.-Specific exaltations of solutions of the sulfones in dioxane.

cannot be attributed unequivocally to across-space homoconjugation. Indications are, from NMR data (33), that the exaltation may be due to intramolecular hydrogen bonding. Whatever the cause, according to Fajans (34), "extensive experimental evidence concerning the molar refraction of inorganic and organic substances leads to the conclusion that derivations from additivity of the Lorentz-Lorenz equation can be considered as an indication and measure of changes in the electronic systems involved. These changes are due to intra- and intermolecular interactions between the parts of the system."

Very few literature references for alkenyl sulfones giving both the refractive index and the density could be found. Price and Gillis (35) reported methyl allyl sulfone and methyl vinyl sulfone as having MRD values of 28.92 and 24.17, respectively, from which derive ΣE values of 0.09 and -0.02. Cope et al. (15) prepared vinyl allyl sulfone and 2-chloroethyl allyl sulfone, which had ΣE values of -0.02 and 0.01, respectively. These values appear to confirm Figure 1, page 22.

The literature was searched in vain for series of dienes (preferably, all prepared by the same person) showing a differential exaltation analogous to the sulfone series. Pentadiene-1,4 (35), hexadiene-1,5 (36), and heptadiene-1,6 (37) had calculated ΣE values of 0.0, 0.07, and -0.15,

respectively. Divinyl ether (38), vinyl allyl ether (39), and diallyl ether (40) had ΣE values of 0.79, 0.18 and -0.80, respectively.

In any case, further work with other similar, but non-hydrogen bonding, series seems appropriate. If it develops that such series show a similar pattern of exaltation changes, perhaps it will also be possible to correlate the degree of cyclopolymerization of a given monomer with its ΣE vs concentration curve.

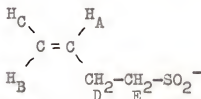
D. Nuclear magnetic resonance spectra

Because the optical exaltations exhibited by the sulfones could not unequivocally be attributed to across-space homoconjugation, NMR spectra thereof were run and information of a preliminary nature was obtained.

In Table 12 are listed the chemical shifts of the A, B, C, D and E hydrogens of n-hexene-1. Also listed are the chemical shifts found for the corresponding hydrogens of the vinyl, allyl and butenyl groups. The difference between the chemical shift for the A hydrogen of n-hexene-1 and, for example, the A hydrogen of the vinyl group (from the table, equal to 1.05 ppm) is caused by the sulfone group.

Examination of Table 12 shows an effect on the allyl α -hydrogen chemical shift (1.75 ppm) which is larger than

TABLE 12
PROTON CHEMICAL SHIFTS OF THE SULFONES



STANDARD; n-hexene-1	A	B	C	D	E
	4.25	5.05	5.13	7.97	8.75-
Vinyl observed shift	3.20	3.90	3.90	--	--
Type	α_a	β	β		
	1.05	1.15	1.23		
Allyl observed shift	4.15	4.60	4.60	6.22	--
Type	β	δ	δ	α	
	0.10	0.45	0.53	1.75	
Butenyl observed shift	4.18	4.95	5.00	6.99	7.52
Type	δ	δ	δ	β	α
	0.07	0.10	0.13	0.98	1.23-

^a α , β , etc., to the sulfone group.

the corresponding effect on the vinyl or butenyl groups (1.05 ppm and 1.23 ppm, respectively).

It appears significant that the double bond and the sulfone group, acting in concert on the α -hydrogens of the allyl group, give rise to a chemical shift which cannot be explained as a merely additive effect. Additionally, comparison shows the effect on the δ -hydrogen chemical shifts (0.45 ppm and 0.53 ppm) to be considerably larger than the effect on the corresponding butenyl shift (0.07 ppm). It is not clear just what factor(s) explains these shifts, though perhaps intramolecular hydrogen bonding figures in the explanation. Such an idea is not unreasonable in view of the observed increased exaltation. It is important to note that the anomalous shifts found for the allyl group are present irrespective of the other group attached to the sulfone; thus, homoconjugation would appear to be ruled out.

CHAPTER IV

SULFONE POLYMERS

A. General

The postulate that the sulfone showing the greatest differential exaltation should show the greatest tendency to cyclopolymerize led to the attempted co- and/or homopolymerization of three members of the series: vinyl allyl sulfone, diallyl sulfone, and vinyl butenyl sulfone.

Originally, no particular difficulty in homopolymerizing diallyl sulfone was expected because of its supposed similarity to the diallyl quaternary ammonium salts. Thus, the earliest, unsuccessful attempts were varied only by changing the solvent system and the concentration of initiator. When an attempt to polymerize diallyl sulfone using no solvent and about 4 weight per cent initiator failed, it was at last recognized that polymerization of any of the sulfones might not be as straightforward as originally anticipated. However, vinyl allyl sulfone did homo-polymerize using dimethyl formamide (hereinafter called DMF) as the solvent and azobisisobutyronitrile as the initiator to give a DMF-soluble product.

In addition to the preparation of the abovementioned homo-polymer, several soluble co-polymers were prepared: diallyl sulfone-acrylonitrile, vinyl allyl sulfone-maleic anhydride, and vinyl butenyl sulfone-maleic anhydride. Only the first was subjected to viscosity measurements: it had an intrinsic viscosity of 0.0772.

IR spectra of the polymers indicated that as polarization of a double bond by the sulfone group decreased in going from vinyl to allyl to butenyl sulfone, the reactivity of that double bond toward free radicals and hence polymerization decreased. IR also showed, in the case of the polymerization of vinyl allyl sulfone, not only that the vinyl group would propagate the chain, but also that the remaining allyl group would not cross-link to adjacent chains, in distinct contrast to the second allyl group of diallyl sulfone, which did react primarily to cyclopolymerize.

B. Attempted homo-polymerization of diallyl sulfone

The first, abortive attempt to prepare a diallyl sulfone homo-polymer was made using dimethyl sulfoxide (referred to as DMSO hereinafter) as the solvent and azobisisobutyronitrile (hereinafter, AB) as the initiator. Diallyl sulfone (1.5124 g) was diluted to 5 ml with DMSO (approximately 2M solution) and 0.0033 g of AB (approximately

0.5 weight per cent of monomer) was dissolved therein. The mixture was then sealed under nitrogen in a 9 mm ID tube and kept at 50° for four days. Comparison of the tube with another tube containing like amounts of diallyl sulfone and DMSO but without initiator showed no apparent viscosity change. At the end of four days, the tube was opened and ether was added. No precipitate formed. Subsequently, the experiment was repeated twice, changing only the initiator concentration (approximately 2 weight per cent and 5 weight per cent, respectively) and the time of exposure (51 days). Again, no polymer was formed. The third and fourth attempts were made using, respectively, acetonitrile and DMF as solvents, and approximately 5 weight per cent AB initiator. No polymer was formed in either attempt. In the final try, 0.5954 g of diallyl sulfone and 0.0257 g of AB were heated under nitrogen in a test tube immersed in a steam bath. The temperature of the mixture was monitored using a thermometer immersed therein. Periodic checks of the temperature for eight hours showed no temperature rise above ambient; the liquid did not change in viscosity. Conclusion: no polymer formed.

C. Vinyl allyl sulfone homo-polymer

Vinyl allyl sulfone was successfully homo-polymerized as follows: vinyl allyl sulfone (2.8591 g) and AB (0.0133 g,

0.47 weight per cent of the monomer), diluted to 5 ml with DMF and sealed in a tube under nitrogen, gave, after thirty days in a constant temperature bath at 50°, 0.6492 g (22.7 per cent conversion) of tan, DMF-soluble polymer, precipitated from the DMF after opening the tube by adding dry ether. The polymer was purified by twice being subjected to this cycle: solution in DMF, precipitation therefrom with dry ether, filtration. Finally, the off-white solid was dried at 50° under vacuum for 24 hours. A comparison of the IR spectrum of a Nujol mull of the polymer with the IR spectrum of the monomer showed the following. The two strong sulfone peaks shifted from 7.6μ and 8.8μ in the monomer to 7.7μ and 8.9μ in the polymer. The vinyl double bond peak at 6.2μ in the monomer was absent in the polymer. The allyl double bond peak at 6.1μ in the monomer shifted to 6.03μ in the polymer. That the sulfone peaks in the polymer are shifted to higher wavelengths can perhaps be explained by the work of Bernard, Fabian and Koch (41), who noted that a solid sulfone absorbs at a frequency $10\text{--}20\text{ cm}^{-1}$ lower than its solution in carbon tetrachloride. The shift of the allyl double bond peak to a lower wavelength hints at greater double bond character, and hence less hydrogen bonding between the α -hydrogens and the sulfone oxygen. In any case, disappearance of the

vinyl double bond peak points to polymerization through the vinyl group.

D. Diallyl sulfone - acrylonitrile co-polymer

A DMF-soluble co-polymer of diallyl sulfone and acrylonitrile was obtained from the sealed tube reaction under nitrogen of diallyl sulfone (2.0410 g, 0.0140 moles) and acrylonitrile (0.6596 g, 0.0124 moles), diluted to 5 ml with tetrahydrofuran and initiated by AB (0.0128 g, 0.47 weight per cent of the monomer present), at 50° for 18 days. A yield of 0.2435 g (9% conversion) of tan-colored polymer was obtained; the polymer was purified by the procedure used for vinyl allyl sulfone. Analysis of the co-polymer: 47.98% C, 5.66% H, 16.25% S and 7.15% N. Mole ratio of sulfone to acrylonitrile, calculated from the per cent sulfur in the polymer: 1 to 0.958. The same ratio, calculated from the per cent nitrogen in the polymer: 1 to 0.976. The IR spectrum, run on a Nujol mull, showed in addition to two strong sulfone peaks at 7.7μ and 8.9μ and a nitrile peak at 4.45μ , a very small double bond peak at 6.15μ . In order to determine whether the peak could be attributed to occluded monomer, the polymer was extracted for six days in a Soxhlet extractor with dry ether: there was no change in the peak height. The polymer had an intrinsic viscosity of 0.0772, as determined using a

Cannon-Ubbelohde semi-micro dilution viscometer. From IR and solubility considerations, it would appear that the polymer formed was largely cyclopolymerized, containing but few pendant allyl groups.

E. Vinyl allyl sulfone - maleic anhydride co-polymers

In an effort to indicate relative reactivity of the comers, vinyl allyl sulfone and maleic anhydride were co-polymerized twice, using equivalent and equimolar amounts, respectively. Each polymerization was carried out in a sealed tube under nitrogen at 50° for 10 days. In the first polymerization, 0.7456 g (0.00760 equivalents) of the anhydride and 0.5116 g (0.00774 equivalents) of the sulfone in 1.2498 g of acetone were initiated by 0.0049 g AB (0.39 weight per cent of monomer present), giving 0.1620 g (12.9% conversion) of a DMF-soluble tan polymer which was purified similarly to the vinyl allyl sulfone polymer. Analysis of the co-polymer: 47.19% C, 5.58% H, 10.68% S, N.E. 154. Mole ratio of sulfone to anhydride, calculated from the per cent sulfur in the polymer: 1 to 1.71. Molecular weight of the repeating unit: 300. Molecular weight calculated from the neutral equivalent: 308. In the second polymerization, 0.5022 g of anhydride (0.00512 moles) and 0.6763 g of sulfone (0.00512 moles) in 1.1853 g of acetone were initiated by 0.0052 g AB (0.44

weight per cent of monomer present) giving 0.1010 g (8.6% conversion) of a DMF-soluble tan polymer which was purified as above. Analysis of the co-polymer: 47.32% C, 5.65% H, 13.29% S, N.E. 171. Mole ratio of sulfone to anhydride, calculated from the per cent sulfur in the polymer: 1 to 1.11. Molecular weight of the repeating unit: 241. Molecular weight calculated from the neutral equivalent: 342. Because of the great disparity between the molecular weight values obtained (probably due to some degree of hydrolysis of the anhydride), no attempt was made to estimate the relative reactivity of the comers.

IR spectra run on Nujol mulls of the two co-polymers were essentially the same in both intensity and position of the peaks: each had two strong sulfone peaks at 7.7μ and 8.9μ , a medium peak at 5.4μ and a strong peak at 5.6μ due to the cyclic anhydride moiety, and a medium carbonyl peak at 5.8μ (due, no doubt, to the carbonyl groups resulting from partial hydrolysis of the polymer). Each, too, had a weak allyl double bond peak at 6.15μ , but no vinyl absorption. Thus, it appears likely that the vinyl allyl sulfone co-polymerized solely via the vinyl group.

F. Vinyl butenyl sulfone - maleic anhydride co-polymers

The vinyl butenyl sulfone, too, was co-polymerized twice: once, using equivalent amounts of the comers and

once using equimolar amounts. Again, the polymerizations were carried out in sealed tubes under nitrogen at 50° for 10 days. In the first polymerization, 0.5024 g (0.00688 equivalents) of the sulfone and 0.6750 g (0.00688 equivalents) of the anhydride in 1.1709 g of acetone were initiated by 0.0058 g AB (0.49 weight per cent of monomer present), giving 0.0384 g (3.3% conversion) of a DMF-soluble, tan polymer which was purified as above. Analysis of the co-polymer: 44.85% C, 5.65% H, 9.74% S, N.E. 203. Mole ratio of sulfone to anhydride, calculated from the per cent sulfur in the polymer: 1 to 1.86. Molecular weight of the repeating unit: 329. Molecular weight calculated from the neutral equivalent: 406. In the second polymerization, 0.7638 g (0.00523 moles) of the sulfone and 0.5009 g (0.00510 moles) of the anhydride in 1.2570 g acetone were initiated by 0.0066 g AB (0.52 weight per cent of monomer present), giving 0.0573 g (4.5% conversion) of a DMF-soluble, tan polymer which was purified as above. Analysis of the co-polymer: 44.18% C, 5.57% H, 11.74% S, N.E. 183. Mole ratio of sulfone to anhydride, calculated from the per cent sulfur in the polymer: 1 to 1.29. Molecular weight of the repeating unit: 273. Molecular weight calculated from the neutral equivalent: 363.

IR spectra run on Nujol mulls of these co-polymers exhibited peaks which were, in position and intensity, essentially the same as those found in the spectra of the vinyl allyl sulfone-maleic anhydride co-polymers. Apparently, then, the polymer chain was again propagated through the vinyl double bond.

CHAPTER V

SUMMARY

A series of six sulfones was collected for the purpose of determining, by certain spectral measurements, whether a postulated homoconjugation occurred.

The series comprised divinyl sulfone, vinyl allyl sulfone, diallyl sulfone, allyl 3-butenyl sulfone, vinyl 3-butenyl sulfone and di-3-butenyl sulfone. Of the series, the first three members had been previously prepared: the divinyl sulfone was obtained commercially and purified by distillation; the vinyl allyl sulfone and diallyl sulfone were prepared by following literature procedures. The last three members, too, were prepared by following well-known literature procedures, but were prepared for the first time.

Originally, it was planned to study the IR spectra, UV spectra and MRD values of the sulfones, but the UV studies could not be consummated: all efforts to run the sulfone UV spectra failed, both here and elsewhere. The IR spectra showed no trends which could be assigned to homoconjugation.

The MRD values and thence the ΣE values of the pure sulfones showed some evidence of a trend attributable to homoconjugation, but the magnitude of the differential exaltation observed was such as to cast doubt on any conclusions drawn. Reasoning that homoconjugation was an intramolecular effect (which possibly was in competition with intermolecular associative effects) led to the preparation of five solutions of diallyl sulfone in dioxane and the determination of the diallyl sulfone MRD at each concentration. No appreciable change in MRD was observed until the diallyl sulfone was between about 5 mole per cent and infinite dilution. On the strength of the results thus obtained, the ΣE values of the several sulfones at the 1.5 mole per cent in dioxane level were determined; the curve thus obtained showed the same maximum corresponding to diallyl sulfone and, additionally, was of such a magnitude that it could not easily be discounted.

Because of the empirical nature of MRD calculations, NMR spectra of the sulfones were run. While the conclusions drawn from the spectra did not support the postulated double bond interaction, the allyl group was found to show certain anomalies (in comparison with the vinyl and butenyl groups) which appeared to support the MRD data.

BIBLIOGRAPHY

1. G. B. Butler and F. L. Ingley, J. Am. Chem. Soc., 73, 895(1951).
2. H. Staudinger and W. Heuer, Ber., 67, 1159(1934).
3. G. B. Butler, R. L. Bunch and F. L. Ingley, J. Am. Chem. Soc., 74, 2543(1952).
4. G. B. Butler and R. L. Goette, ibid., 74, 1939(1952); 76, 2418 (1954).
5. C. Walling, ibid., 67, 441(1945).
6. W. Simpson, T. Holt, and R. Zeite, J. Polymer Sci., 10, 489(1953).
7. R. N. Haward, ibid., 14, 533(1954).
8. R. N. Haward and W. Simpson, ibid., 18, 440(1955).
9. N. Oiwa and J. Ogata, J. Chem. Soc. Japan, 79, 5771 (1957).
10. G. B. Butler and R. J. Angelo, J. Am. Chem. Soc., 79, 3128(1957).
11. G. B. Butler, A. Crawshaw and W. L. Miller, ibid., 80, 3615(1958).
12. G. B. Butler, J. Polymer Sci., XLVIII, 279-289(1960).
13. G. B. Butler and T. W. Brooks, J. Org. Chem., 28, 2699(1963).
14. C. G. Overberger et al., ibid., 19, 1486-9(1954).
15. A. C. Cope, D. E. Morrison and L. Field, J. Am. Chem. Soc., 72, 64(1950).
16. G. Eglington and M. C. Whiting, J. Chem. Soc., 1950, 3650.

17. S. Scherlin and W. Wassilewski, J. Russ. Phys.-Chem. Soc., 60, 1629-32(1928) through Chem. Zentr., 100, I, 2161(1929).
18. H. J. Backer, W. Stevens and N. Dost, Rec. trav. chim., 67, 451-8(1948).
19. L. N. Levin, J. prakt. chem., 127, 77-91(1930) through C.A.: 24, 4257(1930).
20. E. A. Fehnel and M. Carmack, J. Am. Chem. Soc., 71, 92(1949).
21. A. Juvala, Ber., 63, 1992(1930).
22. C. D. Hurd and G. W. Fowler, J. Am. Chem. Soc., 61, 250(1939).
23. A. Pomerantz and R. Connor, J. Org. Chem., 24, 1092(1959).
24. J. R. Alexander and H. McCombie, J. Chem. Soc., 1916(1931).
25. Org. Syn., Coll. Vol. II, p. 571.
26. W. R. Clayton and E. E. Reid, J. Am. Chem. Soc., 64, 908(1942).
27. G. B. Butler and G. D. Price, J. Org. Chem., 24, 1092(1959).
28. S. Glasstone, Textbook of Physical Chemistry, D. Van Nostrand and Co. (Publishers), New York, 1953, p. 529.
29. W. Strecker and R. Spitaler, Ber., 59B, 1775(1926).
30. J. R. Partington, An Advanced Treatise on Physical Chemistry, Longmans (Publisher), New York, 1949, p. 68.
31. J. R. Partington, ibid., p. 69.
32. S. Glasstone, Textbook of Physical Chemistry, D. Van Nostrand and Co. (Publishers), New York, 1953, pp. 531-2.
33. W. S. Brey, Private communication.

34. K. Fajans in Technique of Organic Chemistry, Vol. I, Physical Methods, Part II, Second Edition, Interscience (Publishers), New York, 1949, p. 1171.
35. C. C. Price and R. G. Gillis, J. Am. Chem. Soc., 75, 4750(1953).
36. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, A.P.I. Research Project 44, Carnagie Press (Publishers), Pittsburgh, 1953, p. 62.
37. Ibid., p. 63.
38. Physical Constants of the Principal Hydrocarbons, 3rd Ed., The Texas Co. (Publishers), New York, 1942, p. 49.
39. W. L. Ruigh and R. T. Major, J. Am. Chem. Soc., 53, 2662(1931).
40. R. Paul et al., Bull. soc. chim. France (5), 17, 125(1950).
41. D. Bernard, J. M. Fabian and H. P. Koch, J. Chem. Soc., 1949, 2442.

BIOGRAPHICAL SKETCH

George D. Price was born in Champaign, Illinois on December 5, 1928. He attended public schools in North Carolina, Kansas, Oklahoma, the District of Columbia and Texas, graduating from Alamo Heights High School in 1946.

He entered George Washington University in September, 1947; after the completion of two school years he moved to Gainesville, Florida, where he received the degree of Bachelor of Science in Chemistry in 1951 from the University of Florida.

In August, 1951, he entered the military service, from which he was released in August, 1953. Reentering the Graduate School of the University of Florida in September, 1953, he held first a graduate assistantship and then a research assistantship on an Office of Ordnance Research contract until January, 1956, at which time he received the degree of Master of Science.

Continuing with his graduate studies, he attended school until September, 1959, at which time he accepted a job with the Food and Drug Administration in Washington, D. C.

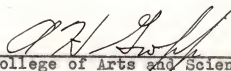
In September, 1962, he resumed his graduate studies in order to complete the requirements for the degree of Doctor of Philosophy.

The author is a member of Gamma Sigma Epsilon, Delta Phi Alpha and Alpha Chi Sigma fraternities.

The author is married to the former Barbara Joan Weidner and is the father of two delightful children, Suzan Heath (2 1/2 yrs.) and William Sheldon (7 mos.).

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.


April 18, 1964

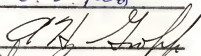

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